

Quasi-chemical Theories of Associated Liquids

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Abstract

It is shown how traditional development of theories of fluids based upon the concept of physical clustering can be adapted to an alternative local clustering definition. The alternative clustering definition can preserve a detailed valence description of the interactions between a solution species and its near-neighbors, *i.e.*, cooperativity and saturation of coordination for strong association. These clusters remain finite even for condensed phases. The simplest theory to which these developments lead is analogous to quasi-chemical theories of cooperative phenomena. The present quasi-chemical theories require additional consideration of packing issues because they don't impose lattice discretizations on the continuous problem. These quasi-chemical theories do not require pair decomposable interaction potential energy models. Since calculations may be required only for moderately sized clusters, we suggest that these quasi-chemical theories could be implemented with computational tools of current molecular electronic structure theory. This can avoid an intermediate step of approximate force field generation.

1. Introduction

Recent molecular calculations [1,2] have suggested in new ways that a chemical perspective can be helpful in computing thermodynamic properties of water and aqueous solutions. This paper follows-up those observations and develops quasi-chemical theories for the thermodynamics of associated liquids.

The most direct antecedent of this effort was the recent calculation of the absolute hydration free energy of the ferric ion (Fe^{3+}) [2]. That calculation used electronic structure results on the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ cluster and a simple, physical estimate of further solvation effects. Those results were organized according to the pattern of a simple chemical reaction and a surprisingly accurate evaluation of the hydration free energy was obtained. A second important antecedent of this work was the recent calculation of the free energy contribution due to electrostatic interactions in liquid water [1]. That work systematically exploited the observed distribution of close neighbors of a water molecule, the distribution of *clusters*, in liquid water in order to obtain an accurate, simple treatment of the thermodynamics of electrostatic interactions in water. The work below is a basic theoretical investigation of the success of these recent calculations.

The developments below are based upon formal theories of association equilibrium that have a long history [3–6]. Formal developments of that kind have been directed in several different ways. One is the study of mechanisms of condensation [6–10]. A second is towards development of theories of molecular liquids in which the molecular species of interest are formed by combination of atoms [11,12]. A third way is towards a theory of associated liquids, like liquid water [13–23]. The latter two goals often overlap and the formal theory is interesting more broadly [23].

For liquid water, the idea of distinguishable association species is a firmly entrenched historical precedent [24,25]. These ideas are called “mixture models” [26–30]. Though the mixture models are common and intuitive ideas, they have never been developed to a satisfactory theoretical conclusion. The available computer simulation data has always suggested that the molecular description of liquid water is more subtle than is typically imagined when mixture models are discussed [31]. It should be noted that the search continues for structural species of special significance in the computer simulation of aqueous solutions [31–37]; but the theoretical connection of such structures to the experimental thermodynamics requires further elaboration. One goal of this work is to clarify the foundations of those ideas and efforts.

The theory developed below is akin to good approximations of historical and pedagogical importance in the areas of cooperative phenomena and phase transitions [38]. In those areas, similar approximations are called Guggenheim, quasi-chemical, or Bethe approximations. However, those treatments typically have been developed for lattice gases, utilizing specialized considerations appropriate for those specialized settings. Our work here emphasizes application to fluids, without initial lattice discretizations, and utilizing modern tools of computational chemistry. As one example, some packing issues that are typically preempted by lattice gas assumptions must be addressed explicitly here. Thus, these derivations and the principal results of them have not been given before.

As a final introductory point, we note the applications of quasi-chemical approximations in treating *lattice* models of water [39–56]. Those efforts may have received less attention than they deserve because of their lack of conventional molecular realism. Indeed, such

calculations sometimes must make arbitrary, prior decisions that may preclude answers to subsequent questions. For example, if pentagonal H-bond rings, or some other specific structure [31,36,37], were crucial for a particular phenomenon, that issue might have to be specifically anticipated and accomodated in typical lattice gas treatments. However, the general success of these approaches should teach us something about how to formulate less restricted theories of liquid water and learning those lessons is also one of the goals of this paper.

2. Theory

We consider two different clustering concepts. The first clustering concept is the more standard [6,9], more global, and more ambitious. Let lower case Greek letters identify basic chemical components. For each component pair $\alpha\gamma$, provide a geometric criterion that determines whether a particular $\alpha\gamma$ pair of particles are clustered. Clusters are then identified in a many-body system by the rule that any pair of particles that satisfy the pair clustering criterion are members of the same cluster. Despite the simplicity of this definition, it holds a fundamental difficulty for theories of liquids: for intuitive clustering criteria, dense liquids are typically past the percolation threshold. The cluster size distribution will include large clusters that have to be directly considered.

The second clustering concept was foreshadowed by the calculations of Hummer, *et al.* [1] and is more local. Focus attention on only one particle. Again consider a definite geometric clustering criterion for all pairs of species types. Then the clusters are only those involving the distinguished particle as the central element, or *nucleus*. These are star-type clusters nucleated on the central element. For example, if the distinguished particle is of type α , the clusters considered are those for which $(0,1,\dots)$ neighbors of the distinguished particle are within the geometric $\alpha\gamma$ clustering criterion for all γ . The size of these clusters will be limited by the maximum coordination number of the distinguished central particle. This will be a practical advantage. But there is the corresponding disadvantage: in the cases that particular extended clusters are expected on a physical grounds to be especially significant, those extended clusters may not have a direct role to play in this theory.

Theories developed for these different clustering concepts will eventually diverge from each other. But they can be characterized by equations of similar form in which cluster properties play a decisive role. The derivation of these equations is our goal.

2.1. Preliminaries

Here we make some preliminary comments that serve to simplify the subsequent derivations and present some of the notation used. A central feature of this development is the potential distribution theorem [57]. For an atomic solute with no internal degrees of freedom this may be expressed as:

$$\rho_\nu \Lambda_\nu^3 = \langle e^{-\Delta U/RT} \rangle_0 z_\nu. \quad (1)$$

$z_\nu = e^{\mu_\nu/RT}$ is the absolute activity of the ν particle and Λ_ν is its thermal deBroglie wavelength. The subscripted brackets indicate the thermal average in the absence of interactions between the solvent and the solute (test particle). Here the averaged property is the Boltzmann factor of the mechanical potential energy of interaction between solvent and solute.

An equivalent description of this bath factor is that $\langle e^{-\Delta U/RT} \rangle_0$ is the average of the Boltzmann factor of the solute-solvent interactions over the thermal motion of the solute and solvent under the condition of no interactions between these two systems. [We note that these results are not limited to pairwise decomposable interactions; the quantity ΔU is the difference between the potential energy of the composite system and that of the separate non-interacting systems.] Permitting the possibility of internal degrees of freedom including orientational degrees of freedom, the required generalization is [57]:

$$\rho_\nu V/q_\nu = \langle e^{-\Delta U/RT} \rangle_0 z_\nu. \quad (2)$$

$q_\nu \equiv q(N_\nu = 1, V, T)$ is the canonical partition function for the system of one molecule of type ν in volume V at temperature T .

Fundamental results below that are central to our derivation can be viewed as formally exact generalizations of this potential distribution expression for the case that molecular clusters form. For those purposes, we will require some elaborations of notation. We suppose that a geometric criterion has been given by which a cluster of type M is recognized and that this criterion is expressed by an indicator function H_M ; $H_M = 1$ when a cluster of type M is formed and zero when it is not. An “ M -clustered” configuration is one for which $H_M = 1$. The results below will involve the canonical partition function, q_M for a cluster of type M ; this is understood to be the partition function of the particles that compose a cluster of type M over the region $H_M = 1$. Suppose that an M -clustered configuration is given and consider placements of particles other than those that are M -clustered. Not all configurations of these additional particles can be permitted without contradiction of the specification that a particular M -cluster is present. A further extension of this notation will use $H_{N|M} = 1$ to indicate that region wherein the N - M other particles in the N -body system are *outside* the clustering condition for an M -cluster. $H_{N|M} = 0$ for positions of those additional species that are not permitted under the condition that the initially specified particles are M -clustered. We then consider bath factors denoted by $\langle e^{-\Delta U/RT} H_{N|M} \rangle_{0,M}$. This will indicate the average over the thermal motion of the M -cluster and the solvent under condition of no interaction between them. The averaged quantity involves the exclusion factor $H_{N|M}$ in addition to the familiar Boltzmann factor of the solute-solvent interactions. This essential exclusion factor then assigns the value *zero* as the weight for those configurations for which the solvent penetrates the M -clustering volume.

2.2. Global Clustering Definition

In order to involve information on clusters, we express the density of interest in terms of cluster concentrations ρ_M . Thus, for the density of the α particles, we would write

$$\rho_\alpha = \sum_M n_{\alpha M} \rho_M \quad (3)$$

where M identifies a molecular cluster considered, $n_{\alpha M}$ is the number of α species in that cluster, and the sum is over all molecular clusters that can form.

The cluster concentrations ρ_M are obtained from

$$\rho_M = (q_M/V) \langle e^{-\Delta U/RT} H_{N|M} \rangle_{0,M} \prod_\gamma z_\gamma^{n_{\gamma M}}. \quad (4)$$

$q_M = q_M(T, V)$ is the canonical partition function covering configurations of an M-cluster [6,9,11,12]. The indicated average utilizes the thermal distribution of cluster and solvent under the conditions that there is no interaction between them. ΔU is the potential energy of interaction between the cluster and the solvent.

Eq. 4 can be derived by considering the grand ensemble. The average number $\langle N_M \rangle$ of such clusters is composed as

$$\begin{aligned} \Xi(\mathbf{z}, T, V) \langle N_M \rangle &= \prod_{\sigma} z_{\sigma}^{n_{\sigma M}} \\ &\times \sum_{\mathbf{N} \geq \mathbf{n}_M} Q(\mathbf{N}, V, T | \mathbf{n}_M) \prod_{\gamma} \binom{N_{\gamma}}{n_{\gamma M}} z_{\gamma}^{N_{\gamma} - n_{\gamma M}}. \end{aligned} \quad (5)$$

Here $\Xi(\mathbf{z}, T, V)$ is the grand canonical partition function; N_{γ} is the total number of γ particles in the system; \mathbf{N} is the set of particle numbers $\{N_{\gamma} \dots\}$ and similarly \mathbf{n}_M is the set of particle numbers for the M-cluster, $\{n_{\gamma M}, \dots\}$; $Q(\mathbf{N}, V, T | \mathbf{n}_M)$ is the canonical ensemble partition function with the constraint that \mathbf{n}_M specific particles are clustered. This constraint means that the general integrand range has been partitioned and this integration is weighted by $H_M H_{N|M}$ for specific \mathbf{n}_M particles clustered. The binomial coefficient $\binom{N_{\gamma}}{n_{\gamma M}}$ is the number of $n_{\gamma M}$ -tuples of γ particles that can be selected from N_{γ} particles. Because of the particle number factors in the summand the partition function there can also be considered to be the partition function for $\mathbf{N} - \mathbf{n}_M$ particles but with an extra, distinguished \mathbf{n}_M objects that constitute the cluster of interest. A natural distribution of those \mathbf{n}_M extraneous objects is the distribution they would have in an ideal gas phase; the Boltzmann factor for that distribution appears already in the integrand of the $Q(\mathbf{N}, V, T | \mathbf{n}_M)$ and the normalizing denominator for that distribution is $q_M(T) \prod_{\gamma} n_{\gamma M}!$. The acquired factorials cancel the denominators of the binomial coefficients. The remaining fragments of the binomial coefficients merely adjust the factorials involved in the definition of $Q(\mathbf{N}, V, T | \mathbf{n}_M)$. Final alignment of the dummy summation variables then leads to Eq. 4.

Combining our preceding results, we obtain

$$\rho_{\alpha} = \sum_M n_{\alpha M} (q_M/V) \langle e^{-\Delta U/RT} H_{N|M} \rangle_{0,M} \prod_{\gamma} z_{\gamma}^{n_{\gamma M}}. \quad (6)$$

This is an equation that might be solved for the absolute activities $\mathbf{z} = (z_{\alpha}, \dots)$ in terms of the densities, cluster partition functions, and the temperature. If the bath contribution is neglected, $\langle e^{-\Delta U/RT} H_{N|M} \rangle_{0,M} = 1$, this is exactly the relation of Eq. 11 of [9]. This is the result that was sought.

Though formally correct, there is a fundamental difficulty with this result. Consider a clustering definition in which particles at near-neighbor distances in solution are clustered. Then the sum will diverge as a percolation threshold is approached by increasing the density of a dilute phase. This is true whether or not cluster interference is neglected. This divergence is sometimes taken as a practical indication of condensation at low temperatures. However, the sum will diverge at similar densities even if no condensation occurs. Thus, this formula is inapplicable to a liquid, traditionally defined, without further considerations.

Notice however that there is a non-trivial special case for which Eq. 6 may be directly applied to a condensed phase and is likely to be helpful. This is the case where species α is a dilute solute and the interest is in the effect of the solvent on μ_{α} . Then we may adopt such

a restricted definition that no solvent-solvent clusters can form. However, at the same time we can define the solute-solvent clustering criteria more physically and study those clusters in which solvent molecules bind to the solute of interest. Those clusters will be finite and the sum of Eq. 6 will involve only a finite number of terms.

2.3. Local Clustering Definition

We will derive the result needed through an indirect argument that utilizes the already derived Eq. 6. We wish to consider non-dilute systems and species for which Eq. 6 does not apply directly. We will find a way to use Eq. 6 by appropriately distinguishing single molecules in this non-dilute phase.

We begin by noting the well-known fact that the chemical potential, say μ_α , can be divided into ideal and interaction parts. The ideal contribution takes the form $RT \ln \rho_\alpha + \text{constant}$ where the constant might be calculated on the basis of molecular properties; see Eq. (1). The first step in our argument is the specification that the theory need only determine the interaction part of the chemical potential since the ideal contribution is well-known. To determine the interaction part of the chemical potential we distinguish a single molecule of type α and study its condition in solution. This is natural; for example a simulation calculation might select a particular α molecule and perform charging or uncharging calculations, or determine distributions of binding energies experienced [1]. When an α molecule is selected for the purposes of calculation of the interaction part of μ_α it can be treated as a solute at the lowest non-zero concentration, as a solitary impurity. We will denote the chemical potential of this distinguished solute as $\mu_{\alpha'}$, remembering that the interaction part of $\mu_{\alpha'}$ will be the same as the interaction part of μ_α . For a dilute solute, we can define clustering criteria, as anticipated above, so that no solvent-solvent clustering occurs as defined, but the definition of clustering of solvent molecules about the distinguished α solute is naturally included. Eq. 6 then does apply to the calculation of $\mu_{\alpha'}$.

The modifications of Eq. 6 for this case are two: First, the stoichiometric coefficients of Eq. 3, that appear later in Eq. 6, are all one (1); since the distinguished solute is at the lowest non-zero concentration there cannot be more than one such solute in any cluster. The right side of Eq. 6 is precisely proportional to $z_{\alpha'}$. Second, all clusters are of star type, that is, AB_n with the distinguished solute at the center.

Before finally writing the desired result, we ask again about the ideal contribution to $\mu_{\alpha'}$ and to μ_α . This ideal contribution is reflected in the density on the left of Eq. 6. For μ_α that density is the physical value and is part of the definition of the problem. For $\mu_{\alpha'}$, if our argument were taken literally, that density on the left would be $\rho_{\alpha'} = 1/V$. Replacement of that value by ρ_α , and on the right simultaneously $z_{\alpha'}$ by z_α , would merely readjust $\mu_{\alpha'}$ up to μ_α through a final assessment of the ideal contribution. Thus, we have

$$\rho_\alpha = \sum_{M(\alpha)} (q_M/V) \langle e^{-\Delta U/RT} H_{N|M} \rangle_{0,M} \prod_{\gamma} z_{\gamma}^{n_{\gamma M}}. \quad (7)$$

The sum is over all clusters $M(\alpha)$ that can form on an α nucleus.

A practical example of the importance of the clustering definition may be helpful. Recent work on clusters of a chloride ion with water has suggested that the preferred disposition of the chloride ion may be near the surface of the cluster [58]. This interesting point is unlikely to be decisive for the application of this cluster formula to the study of the solvation of the

chloride ion in liquid water. The cluster definitions here require that the chloride be the *nucleus* of a star-type cluster. That would permit the chloride ion to access the physical surface of a droplet only for small clusters and larger clusters are likely to be decisive in establishing the bulk phase thermodynamics of the aqueous solutions containing chloride ions.

2.4. Cluster Interference

This paper will develop the local clustering alternative; the global clustering results will serve as contrast. The issue of cluster interference is different in the two cases. The development requires a complete and unique partitioning of phase space into regions characterized by a specific cluster population. For each proper configuration, the definition uniquely assigns elementary particles to clusters. With this characteristic, we then formally regard the cluster populations as supplementary integration (summation) variables, first integrating over configurations with a specific constraint of a specific cluster population, then summing over permitted cluster populations. Cluster interference is a simple implementation of the constraint. If a particular cluster of type M is specified then configurations that violate the specification cannot be allowed. As a particular example, suppose that an A_n cluster is under consideration. Then some configurations for which an additional A particle approaches the A_n cluster must be excluded; otherwise configurations of A_{n+1} clusters would become confused with configurations of A_n clusters. In the notation above these constraints are lumped into the factors $\langle e^{-\Delta U/RT} H_{N|M} \rangle_{0,M}$ through rigid exclusion interactions. It is in these bath factors and the cluster partition functions q_M that cluster interference is expressed.

For the global clustering development, these cluster interference contributions are complicated because they depend on all the cluster sizes and shapes. However, the global clustering result Eq. 6 is fundamentally inapplicable to liquids.

In contrast, for the local clustering development cluster interference is much simpler. If we specify that a cluster of type A_n is considered, we must only require that the $n-1$ particles are within the clustering volume v of a distinguished molecule (easy to do) and that no more than $n-1$ additional particles are there. This latter factor is familiar from studies of packing problems in liquids [59] and in the potential distribution factor it involves the probability that the clustering volume v is *empty* of solvent species [60]. We can consider the condition that the clustering volume is empty of solvent molecules by introducing the probability for that event, p_0 . The van der Waals approximation $p_0 \approx (1 - \rho v)$ should be qualitatively satisfactory and provides definiteness to the discussion. Thus, within the local clustering approach, cluster interference is completely expressed by the form

$$\frac{\rho_\alpha}{z_\alpha} = p_0 \sum_{M(\alpha)} (q_M/V) \langle e^{-\Delta U/RT} \rangle_{0,M}^* \prod_\gamma' z_\gamma^{n_\gamma M}. \quad (8)$$

Now the well-decorated term $\langle e^{-\Delta U/RT} \rangle_{0,M}^*$ indicates the average over the thermal motion of the M-cluster and solvent under that condition that the only interactions between them rigidly enforce the exclusion of the solvent from the M-clustered volume. We have factored out the z_α because this quantity must be present in each term, because the ratio ρ_α/z_α is a standard form, and because the distinguished α particle that is the nucleus of the cluster requires a different treatment than do the particles on the periphery of the star. The notation

\prod'_γ means that the term for the species nucleating the cluster should be stricken from the product. Though this result is formally complete, an approximate theory will have to be utilized for p_0 in specific applications.

2.5. Quasi-chemical Approximation

A theory with quasi-chemical form is

$$\langle e^{-\Delta U/RT} \rangle_{0,M}^* \prod_\gamma ' z_\gamma^{n_{\gamma M}} \approx \prod_\gamma ' \{ \rho_\gamma(V/q_\gamma) \}^{n_{\gamma M}}. \quad (9)$$

This replacement is motivated by the desire to replace the ‘bare fields’ $\ln z_\sigma$ with effective fields, by the recognition that Eq. 2 provides a pattern for that replacement, and by the appreciation that the bath contributions might reasonably factor for species on the “surface” of the cluster.

Note that the list of clusters $M(\alpha)$ should include the monomer. One term in this list for Eq. 8 will have $q_M = q_\alpha$. Thus, we can write

$$\frac{\rho_\alpha V}{z_\alpha q_\alpha} \approx p_0 \left(1 + \sum_{M(\alpha)} ' K_M(T) \prod_\nu ' \rho_\nu^{n_{\nu M}} \right), \quad (10)$$

where

$$K_M(T) = \frac{q_M/V}{\prod_\nu \{ q_\nu/V \}^{n_{\nu M}}} \quad (11)$$

and the sum of Eq. 10 is over the list of possible star clusters nucleated by an α species but *not* including the monomer cluster. This theory deserves the appellation “quasi-chemical” because the coefficients $K_M(T)$ are the chemical equilibrium ratios for the formation of star clusters in a dilute gas [61]. Note, however, that the factor p_0 will be essential for description of packing effects and thus for predictions of thermodynamic properties of condensed phases. The thermodynamic quantity sought is the chemical potential

$$\mu_\alpha \approx RT \ln[\rho_\alpha V/q_\alpha] - RT \ln[p_0 (1 + \sum_{M(\alpha)} ' K_M(T) \prod_\nu ' \rho_\nu^{n_{\nu M}})]. \quad (12)$$

This formula makes the conventional, helpful separation between the contributions of inter-molecular interactions and the non-interaction (ideal) terms; see Eq. 2. Quantities such as p_0 and the $K_M(T)$ depend on parameters that define the clustering circumstances. But, since the physical problem is independent of those parameters, the theory should be insensitive to them if it is to be satisfactorily accurate.

2.6. Discussion

The formal results Eqs. 7 and 8, and the approximation Eq. 12 are believed to be new. The approximation Eq. 9 attempts to eliminate the complicated bath contributions. These quantities are formally well-understood and can be formally analyzed with Mayer mathematical cluster expansions or functional analyses. Here we discuss physically what’s neglected. For

dilute solutions where the solvent activities are known separately, Eq. 8 may be used directly and the issues that follow here are not relevant. This was the pattern of the motivating calculations [1,2].

Eq. 9 assumes that each activity factor may be replaced using the relation Eq. 2 with no account of the interference between different sites that is formally expressed in the left-side of Eq. 9. This might be correct for idealized circumstances, e.g. a “Bethe lattice” (no cycles). [An alternative derivation based upon diagrammatic arguments makes it clear that this is a *tree* approximation.] But for more realistic continuous problems there are two sources of that interference. Firstly, different peripheral sites on the star cluster can interfere with one another. This effect arises because solvent molecules can interact with two or more surface sites jointly. The organization of the problem here is designed to mitigate that interference between different surface species. Secondly, “through solvent” interference between a peripheral site and the nucleus of the cluster arises when solvent molecules can interact with a surface surface sites and the nucleus or cluster volume jointly. Eq. 9 neglects both of these effects.

We reiterate that the quantities neglected by the approximation Eq. 9 are well understood formally. Thus, in specific applications it should be practical to augment this approximation with additional contributions that are understood physically and theoretically. An example should serve to clarify this point. There has been significant recent interest in primitive electrolyte solution models under circumstances where ion pairing and clustering is acknowledged to be of primary significance [62]. The formal developments here apply also to ion clustering in electrolyte solutions. However, where non-neutral clusters are important the approximation Eq. 9 must be at the least augmented to treat long range interactions, likely following a random phase approximation.

A more specific example is given by the study of the hexa-aquo ferric ion, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ reported in Reference [2]. The data given there allow us to estimate the error of the neglect of long-ranged interactions, Eq. 9. That neglected contribution would be about 391 kcal/mol, or 38% of the value inferred from experiment for interaction part of $\mu_{\text{Fe}^{3+}}$. [See Table IV of that report but note that the packing contribution here present as p_0 was neglected in that previous study.] Thus, for ionic solutes in particular, further consideration of coulomb ranged interactions will be necessary. Though the physical estimate given for the hexa-aquo ferric ion example [2] was natural and surprisingly accurate, the value 391 kcal/mol was essentially empirically derived. To do better than that, the present approach must be extended to produce the dielectric constant of the liquid in order to assess screening of electrostatic interactions. Since the this approach has a conceptual overlap with the Onsager-Kirkwood [63,64] development of the theory of dielectrics that subsequent step should be natural. We note, however, that the present hybrid approach will improve the treatment of negative ions in solution, such as the Cl^- ion which was a remaining difficulty for the multistate gaussian model [1].

Finally, the hexa-aquo ferric ion example emphasizes that current electronic structure software can routinely produce $K_M(T)$ in a harmonic approximation. Other recent examples include the work of references [65–68]. This encourages us to anticipate that further developments will permit implementation of these theories without an intermediate effort to obtain approximate force field models. In the near term, this approach should at the least offer a direction for improvement of electronic structure calculations on solution species,

calculations that might presently rely solely on dielectric continuum models.

3. Conclusions

The traditional development of theories of fluids based upon the concept of physical clustering can be adapted to an alternative local clustering definition. The alternative clustering definition can straightforwardly preserve a detailed valence description of the interactions between a solution species and its near-neighbors, *i.e.*, cooperativity and saturation of coordination for strong association. These clusters remain finite even for condensed phases. The simplest theory to which these developments lead is analogous to quasi-chemical theories of cooperative phenomena. The present quasi-chemical theories require additional consideration of packing issues because they don't impose lattice discretizations on the continuous problem. These quasi-chemical theories do not require pair decomposable interaction potential energy models. Since calculations may be required only for moderately sized clusters, we anticipated that these quasi-chemical theories could be implemented with computational tools of current molecular electronic structure theory.

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